

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)
23-09-2003

2. REPORT TYPE

Technical Viewgraph Presentation

3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

Polynitrogen Chemistry

5a. CONTRACT NUMBER

F04611-99-C-0025

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER	
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5d. PROJECT NUMBER

DARP

5e. TASK NUMBER

A205

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

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10. SPONSOR/MONITOR'S ACRONYM(S)	
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11. SPONSOR/MONITOR'S
NUMBER(S)

AFRL-PR-ED-VG-2003-240

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

For presentation at the 2nd Advanced Energetics Technology Exchange taking place at the Aberdeen Proving Grounds, MD, from 22-26 September 2003.

14. ABSTRACT

20031017 120

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON
Leilani Richardson

a. REPORT

b. ABSTRACT

c. THIS PAGE

Unclassified

Unclassified

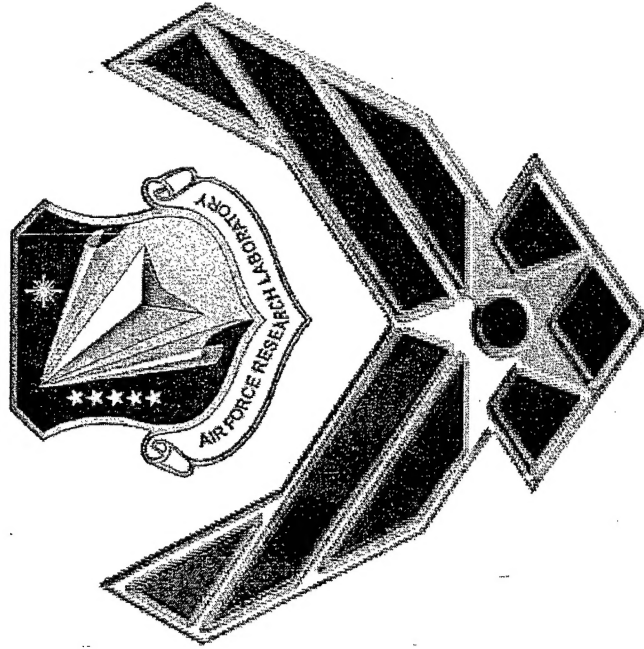
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19b. TELEPHONE NUMBER (include area code)
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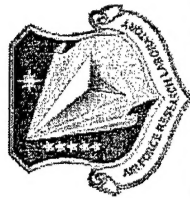
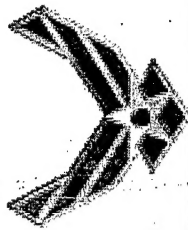
Karl Christe

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Air Force Research Laboratory,
Edwards AFB,**

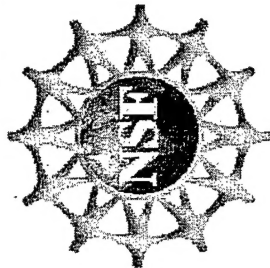
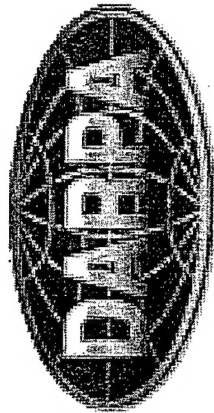
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University of Southern California

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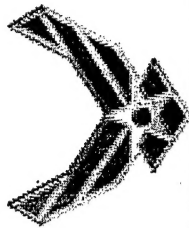
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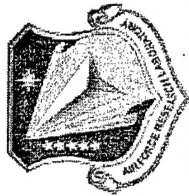
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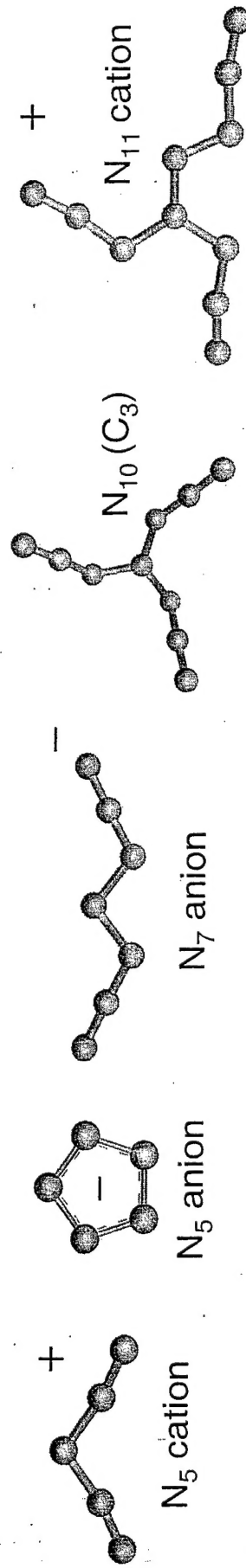
Program Objectives



Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen compounds

Technical Approach:

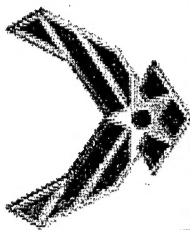
- Exploit synergism between theory and synthesis
- ♦ Use calculations to identify the most promising candidates and predict their properties
- ♦ Use experimental expertise to design synthesis approaches, prepare novel compounds, and characterize products



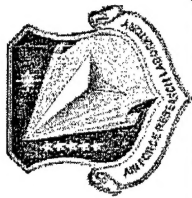
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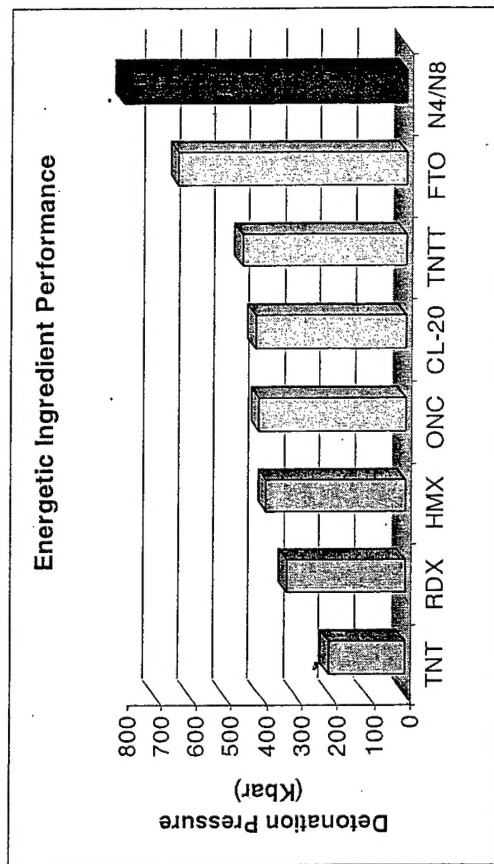
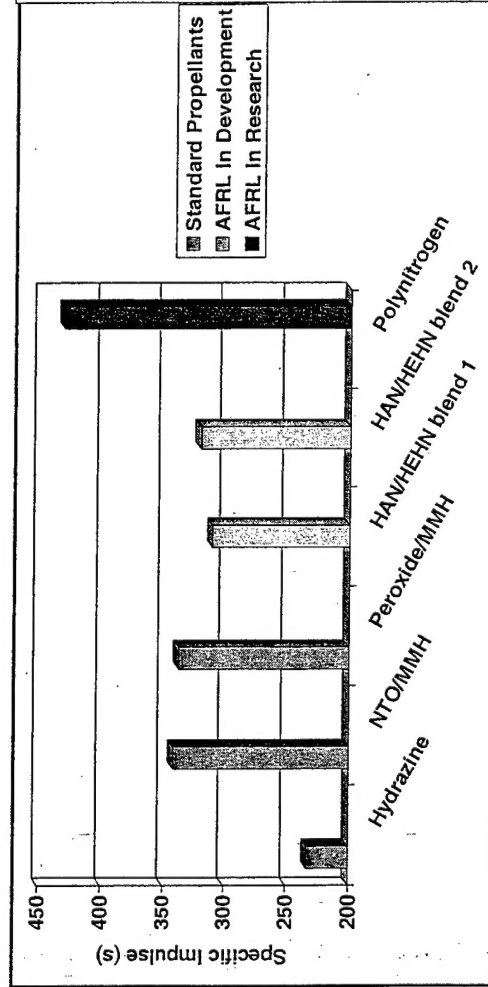
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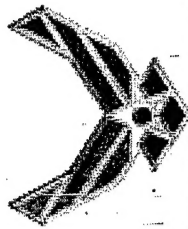
Performance of Polynitrogen as Monopropellants and Explosives



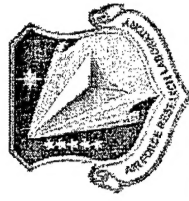
The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants



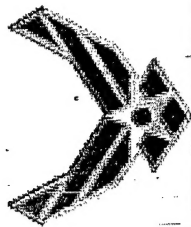
Polynitrogens would also have great potential as high-performance explosives, with performance 2-3 times that of current materials



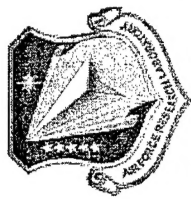
Previous Accomplishments



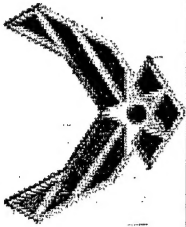
- Discovered N_5^+ , the first new stable polynitrogen species in more than 100 years and only the second known stable homonuclear polynitrogen species
- Prepared and characterized $N_5^+AsF_6^-$, $N_5^+SbF_6^-$, $N_5^+Sb_2F_{11}^-$, $N_5^+B(CF_3)_4^-$, $N_5^+SnF_5^-$, and $(N_5^+)_2SnF_6^{2-}$
- Scaled up $N_5^+SbF_6^-$ production to 5 g level
- Obtained experimental evidence for instability of $N_5^+N_3^-$, $N_5^+NO_3^-$, and $N_5^+ClO_4^-$
- Prepared and characterized the N_3NOF^+ cation
- Experimentally detected the pentazolate anion, *cyclo*- N_5^- , by electrospray negative ion mass spectroscopy



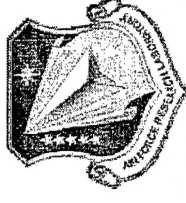
Recent Results



- Synthesis of $N_5^+HF_2^- \cdot nHF$, $N_5^+PF_6^-$, $N_5^+BF_4^-$, and $N_5^+[P(N_3)_6]^-$
- Reactions of NF_4^+ and $N_2F_3^+$ with HN_3
- FN_5
- Bulk Synthesis of N_5^-
- Can $N_5^+N_3^-$ and $N_5^+N_5^-$ exist?
- Polyazido compounds



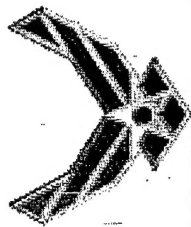
Synthesis of $N_5^+HF_2^- \cdot nHF$



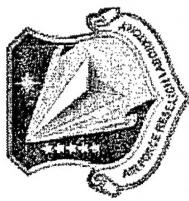
- Original plan was the metathetical synthesis of $N_5^+N(CF_3)_{3/2}^-$
- $$N_5^+SbF_6^- + Cs^+N(CF_3)_{3/2}^- \xrightarrow{HF, -78\text{ C}} CsSbF_6 \downarrow + N_5^+N(CF_3)_{3/2}^-$$
- Filtered off $CsSbF_6$ and pumped off all volatiles at -64 C
- Obtained clear colorless liquid, Raman of which showed only bands due to N_5^+
- Actual reactions



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Synthetic Potential of $N_5^+HF_2^-$



- By analogy with $NF_4^+HF_2^-$, the $N_5^+HF_2^- \cdot nHF$ salt is a very useful reagent for the preparation of many new N_5^+ salts in high purity



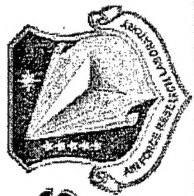
- Any Lewis acid that has a higher F^- affinity than HF (45 kcal/mol) should be able to displace HF
- Principle was successfully demonstrated for



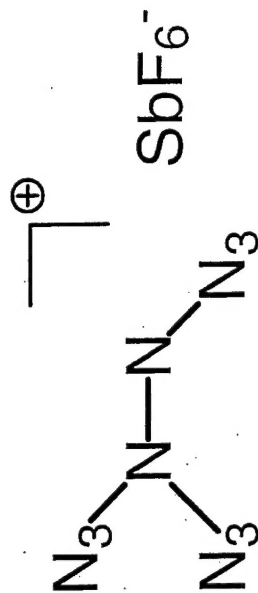
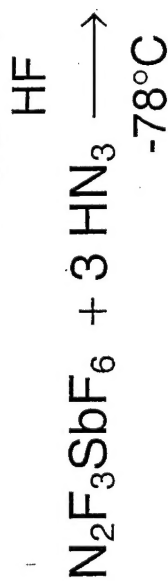
and $N_5^+BF_4^-$ and $N_5^+PF_6^-$ were isolated as stable solids and characterized



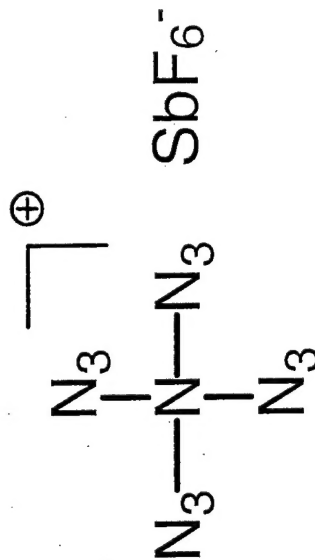
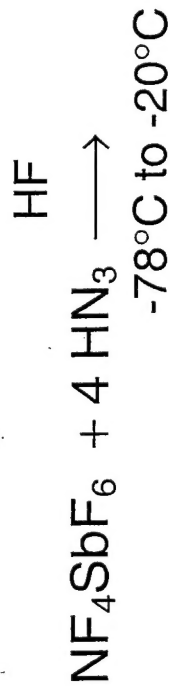
Attempted Syntheses of N_x^+ Species ($x = 11, 13$)

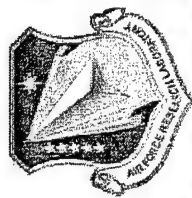


- Desired product $(N_3)_2NN(N_3)SbF_6$



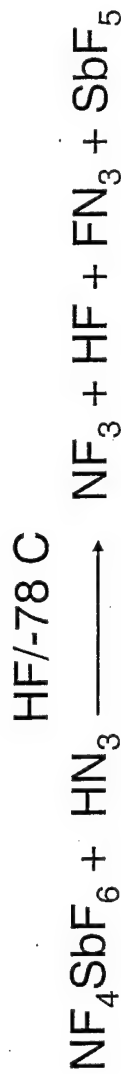
- Desired product $N(N_3)_4SbF_6$



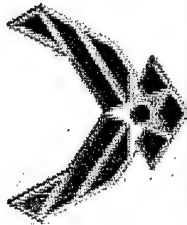


Reaction of NF_4^+ with HN_3

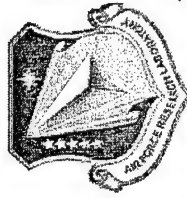
- Reaction of NF_4^+



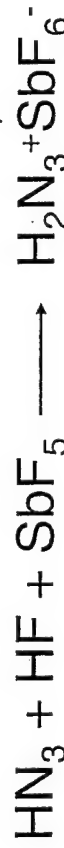
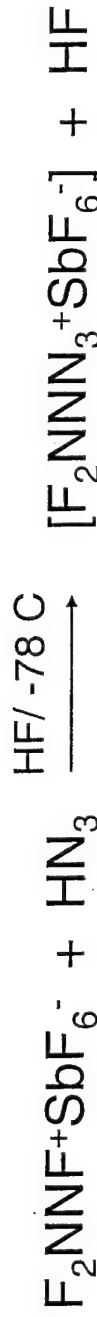
- NF_4^+ acts as a fluorinating agent, fluorinating HN_3 to FN_3



Reaction of $N_2F_3^+$ with HN_3



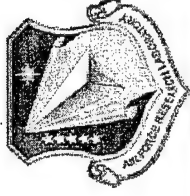
- Reaction of F_2NNF^+



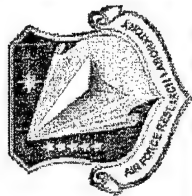
- The absence of $N_2F^+SbF_6^-$ or $N_5^+SbF_6^-$ in the product favors this substitution mechanism over an oxidation reaction with N_2F_2 formation



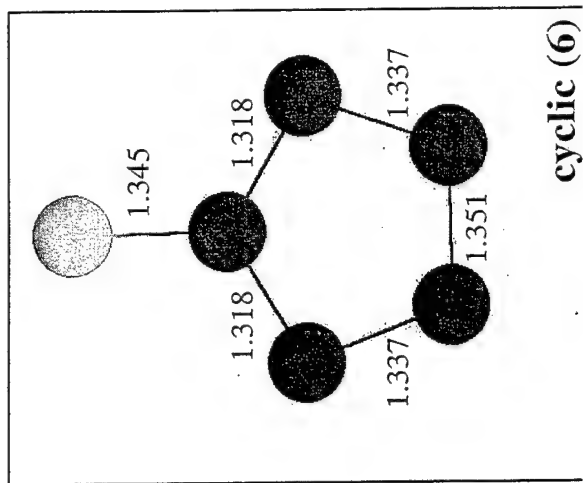
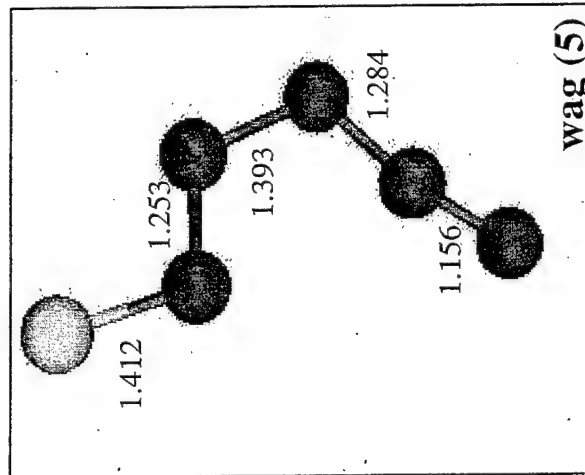
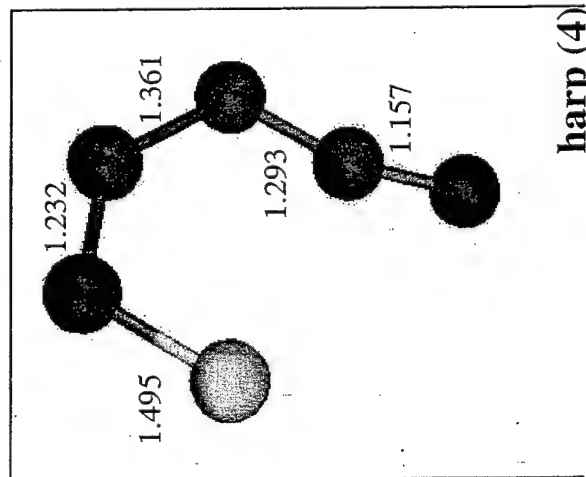
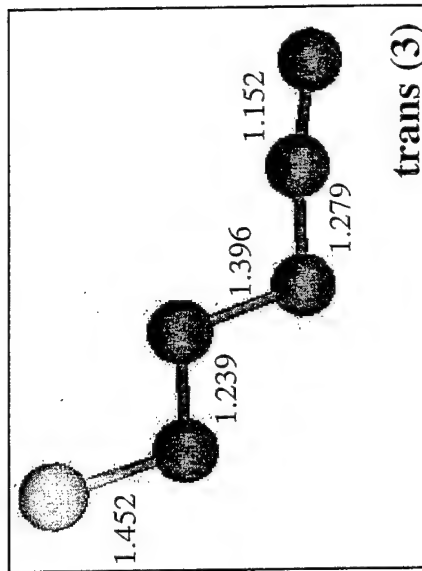
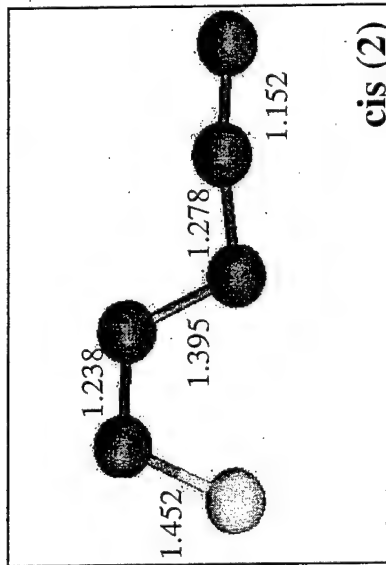
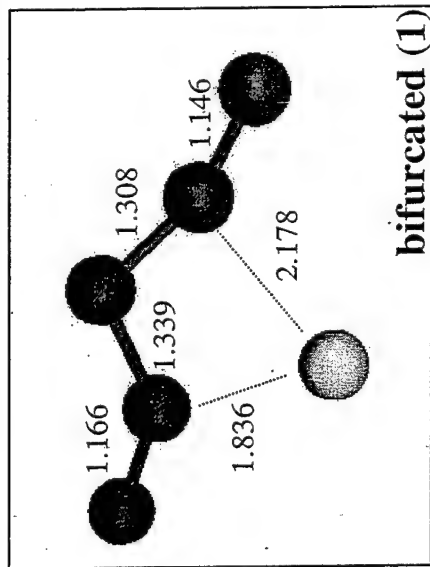
FN_5



- Controlled decomposition of $(\text{N}_5^+)_2\text{SnF}_6^{2-}$ to $\text{N}_5^+\text{SnF}_5^-$ and " FN_5 " allowed us to search for FN_5 by dynamic FT-IR spectroscopy
- Observed only FN_3 and its decomposition products (N_2F_2 and NF_3)
- Theoretical study was carried out showing six stable isomers differing by about 6 (MP2) and 10 (CCSD(T)) kcal/mol in energy
- Intrinsic reaction coordinate and dynamic reaction path calculations were used to study the isomerization and decomposition of FN_5
- Based on a Rice-Ramsperger-Kassel-Marcus analysis, the lifetime of FN_5 was estimated to be in the nanosecond range explaining our failure to observe FN_5 experimentally



Six FN_5 Isomers ($MP2/6-31++G(d,p)$)



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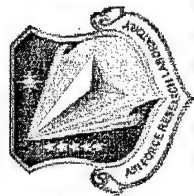
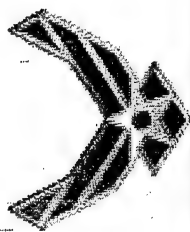
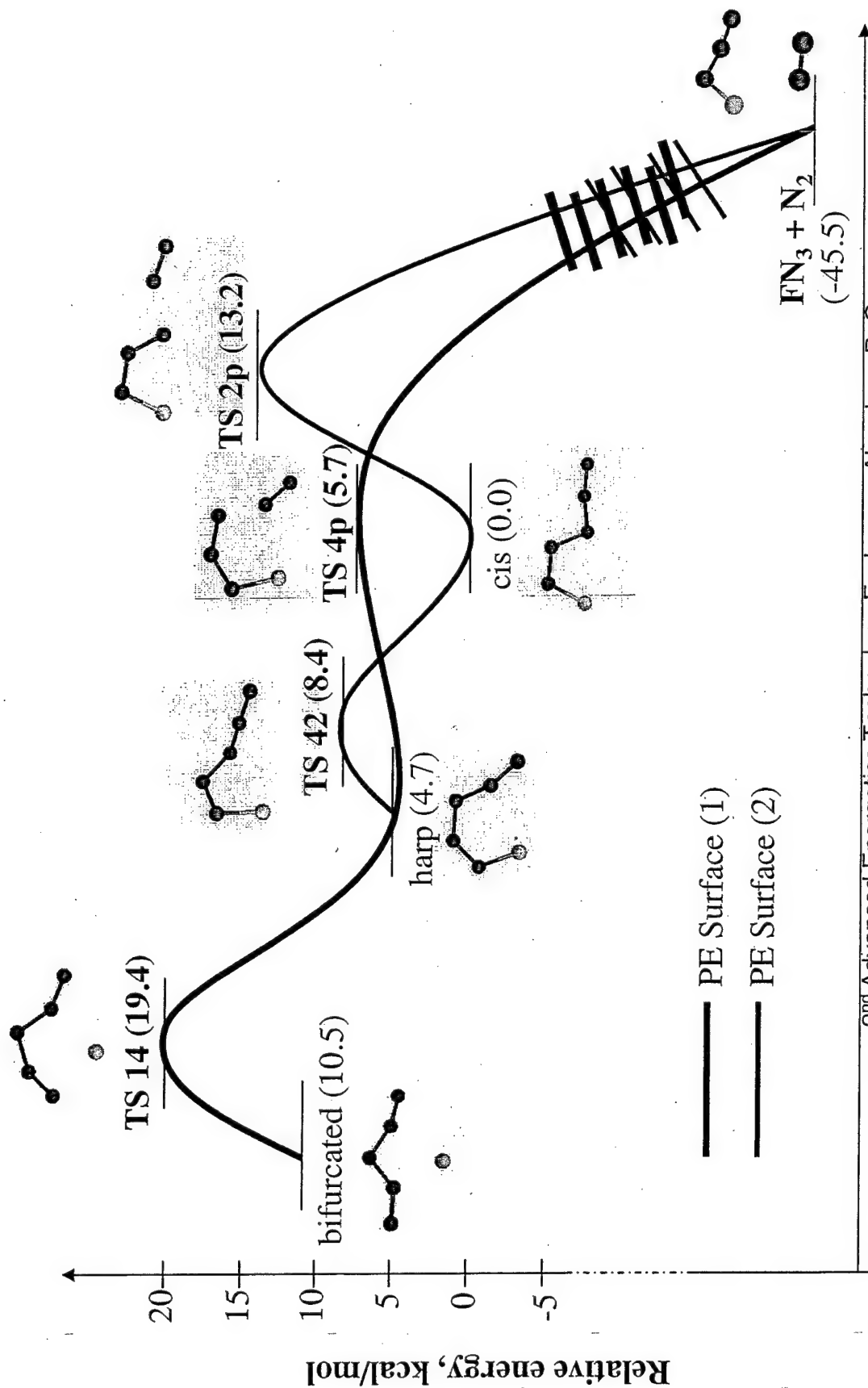
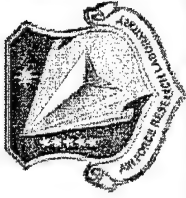


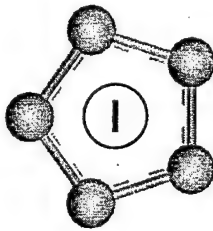
Figure 8. Relative isomerization/decomposition PESs with FN_5 isomers (reference = *cis*-isomer)



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 *Energies: CCSD(T)/aug-cc-pVTZ with ZPE
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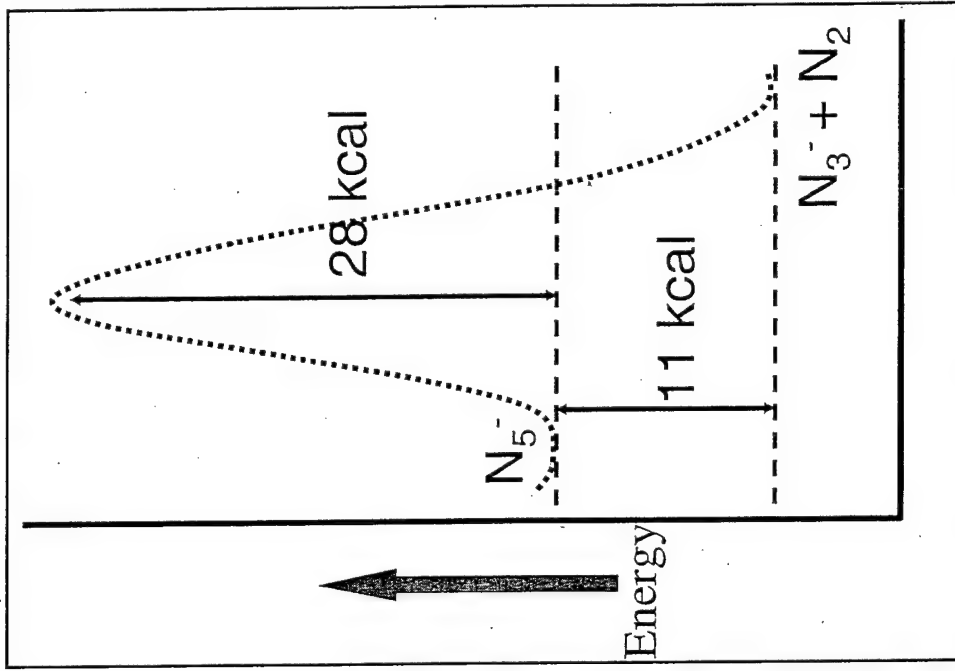


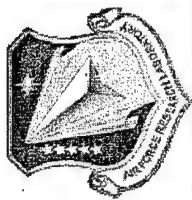
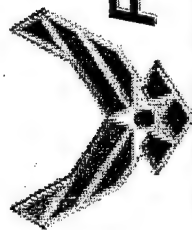
Pentazolate Anion



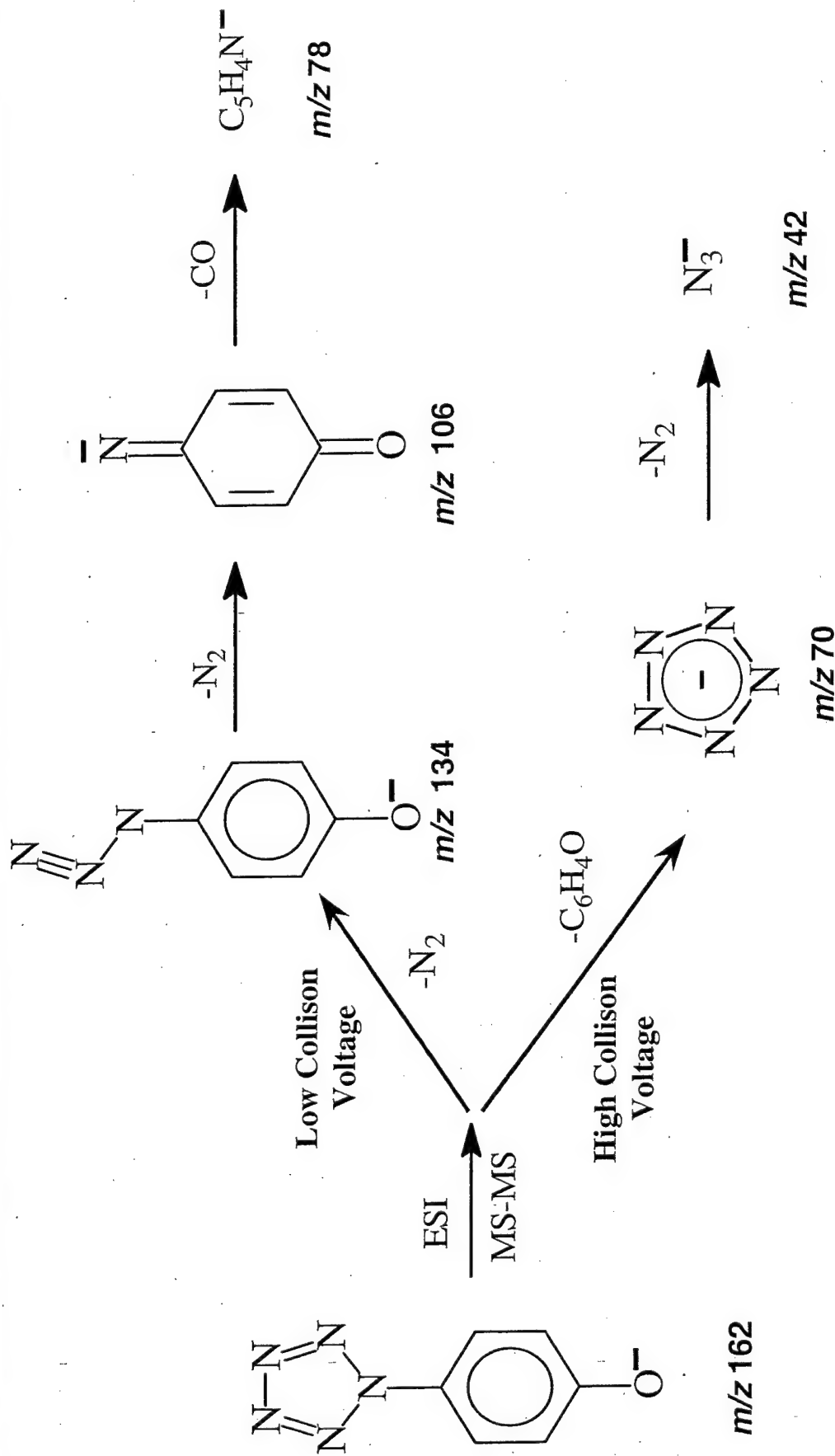
Pentazolate anion (N_5^-)

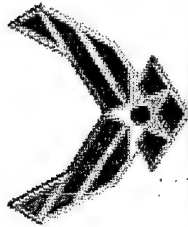
- Theoretical calculations (Nguyen and Ha, and Bartlett et al) predicted that this anion has a 28 kcal/mol activation energy barrier for decomposition, a high vertical ionization potential of 5.58 eV, and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic
- Aryl substituted pentazoles had been known for 40+ years, but all previous attempts to isolate HN_5 or N_5^- had failed



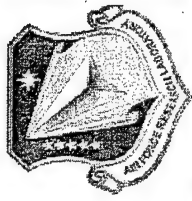


Identification of N_5^- by ES-IMS of para-Pentazolyphenolate (Angew. Chem. 2002, 41, 3051)

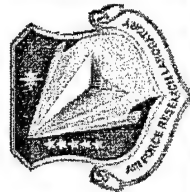




Search for a Bulk Synthesis of N_5^-

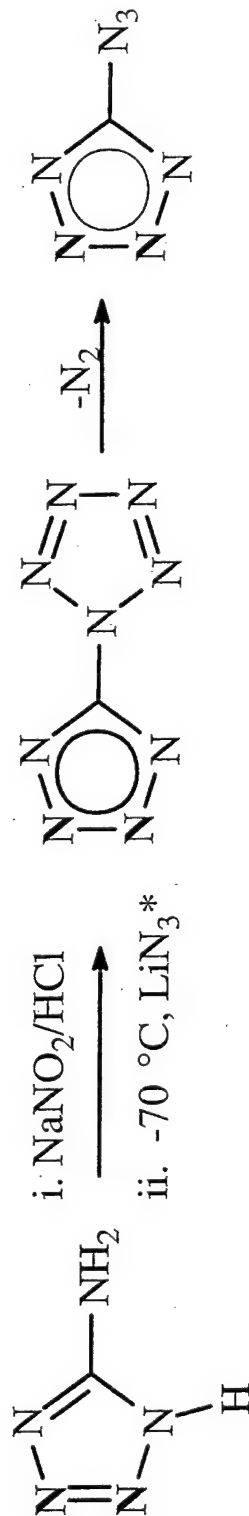


- Nitrogen NMR studies are ideally suited for screening reactions, and we and others (Butler et al) have observed N_5^- by ^{15}N NMR at low-temperature in CH_3OH solutions during the cleavage of pentazolyphenolate
- We have also demonstrated by ^{15}N NMR that azolyl substituents are better leaving groups



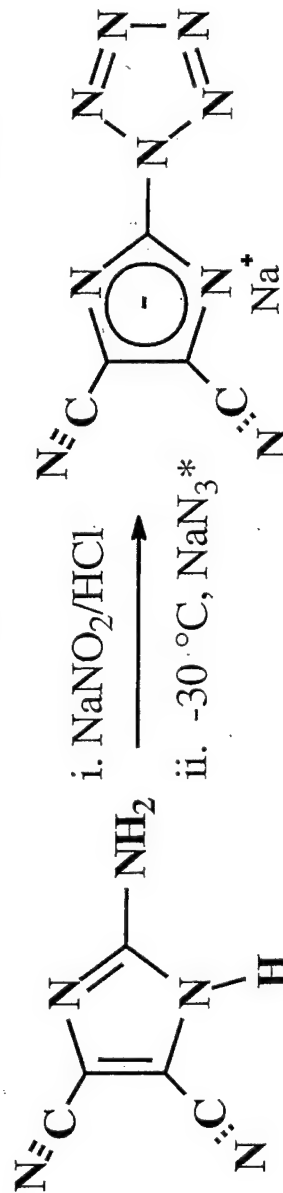
Pentazoles with Heterocyclic Substituents

- Tetrazolyl system is unstable above -70°C and the pentazole ring rapidly decomposes to liberate N_2 gas.



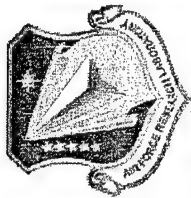
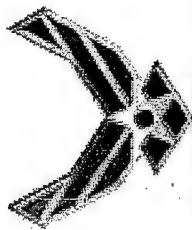
A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* **2002**, 41, 906-912

- By comparison, the pentazole derivative of 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30°C)

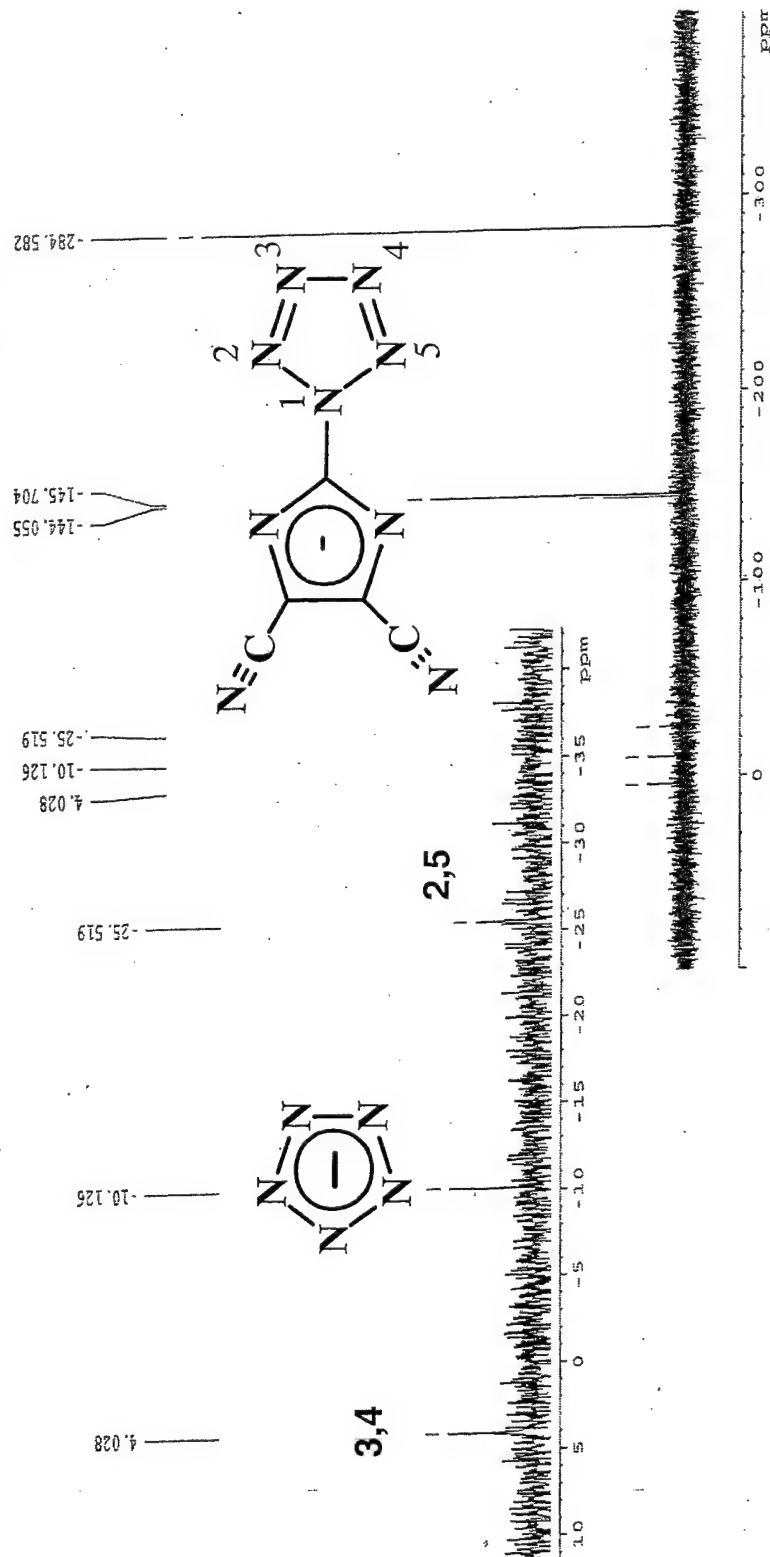


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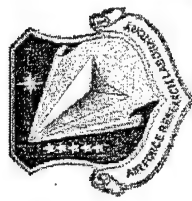
^{15}N NMR of N_5^- in Solution



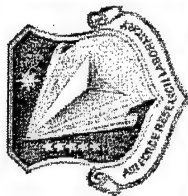
➤ ^{15}N NMR shows a peak at -10 ppm (-30 °C), which slowly decomposes to form N_2 and azide ion. This peak is also observed upon adding OH^- to the solution of arylpentazoles at -30 °C.



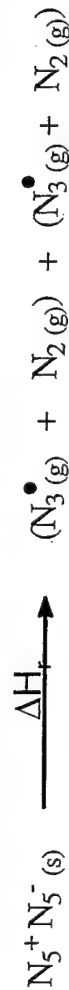
Existence of $N_5^+N_3^-$ and $N_5^+N_5^-$



- Previously published stability predictions and energy density calculations for $N_5^+N_5^-$ and $N_5^+N_3^-$ are incorrect due to the use of vertical instead of adiabatic electron affinity and ionization potentials. This can cause huge errors.
- The correctness of our approach was demonstrated by experimentally bracketing the electron affinity of N_5^+ (10.52-11.48 eV) which agrees well with our calculated adiabatic value of 10.55 eV, but not with the vertical value of 6.04 eV.
- We have calculated highly accurate enthalpies of formation and adiabatic electron affinities and ionization potentials for N_3 , N_3^- , N_5^+ and N_5^- from total atomization energies.
- The stability of an ionic solid is governed by the sum of the first ionization potential of the anion, the electron affinity of the cation, and the lattice energy, as shown by the following Born-Haber cycles.

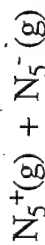


Born-Haber Cycles for $N_5^+N_3^-$ and $N_5^+N_5^-$



$$-61.4 \pm 5.7$$

$$\Delta H_L = 134 \pm 5$$



$$IP (N_5^\bullet) = 47.9 \pm 2$$

$$EA (N_5^+) = -243.3 \pm 2$$

- Problem with the N_5 ions:

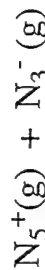
Both, cyclic and catenated N_5 radicals are vibrationally unstable and decompose without barrier to N_3 . Because N_3 has a barrier, $N_5^+N_3^-$ is less unstable than $N_5^+N_5^-$

- For a salt to be stable, ΔH_f must be zero or positive



$$-36.1 \pm 7.5$$

$$\Delta H_L = 146 \pm 7$$

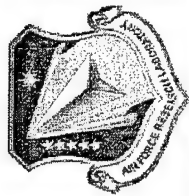


$$IP (N_3^\bullet) = 61.2 \pm 2$$

$$EA (N_5^+) = -243.3 \pm 2$$

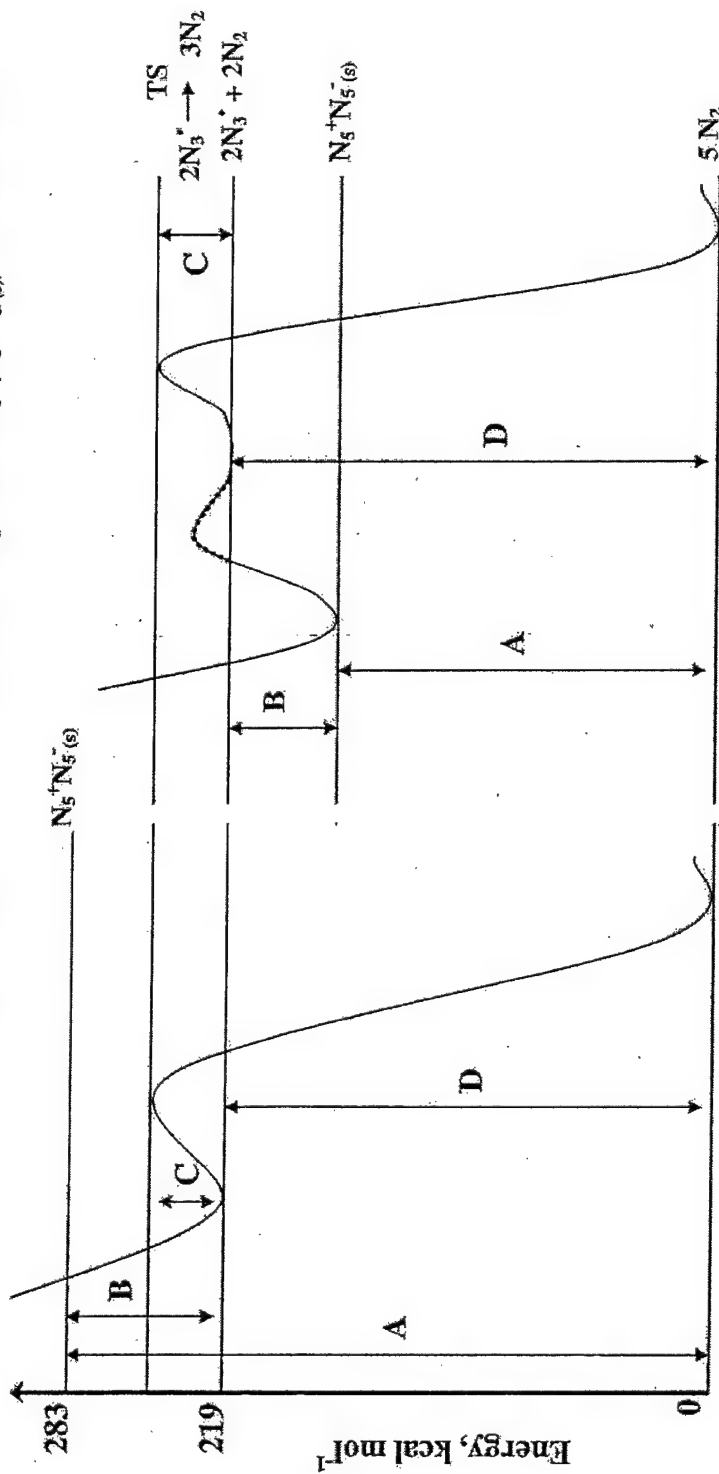


Potential energy curves for $N_5^+N_5^-$



NEGATIVE B VALUE, KINETICALLY UNSTABLE, REPRESENTS CALCD VALUES

POSITIVE B VALUE AND KINETIC STABILITY WOULD REQUIRE $\Delta H_f(N_5^+N_5^-) \approx 180 \text{ kcal/mol}$



$$A = \Delta H_f(N_5^+N_5^-)$$

$$B = \Delta H_f(N_5^+N_5^-) \rightarrow 2N_3(g) + 2N_2(g) = U_L(N_5^+N_5^-) + 2RT + IP(N_5^-) - EA(N_5^+)$$

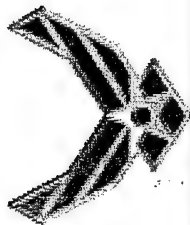
$$C = \text{Activation energy barrier for decomposition of } 2N_3(g) \rightarrow 3N_2(g)$$

$$D = \Delta H_f(2N_3(g) \rightarrow 3N_2(g))$$

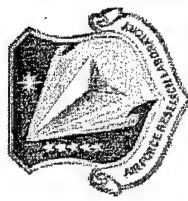
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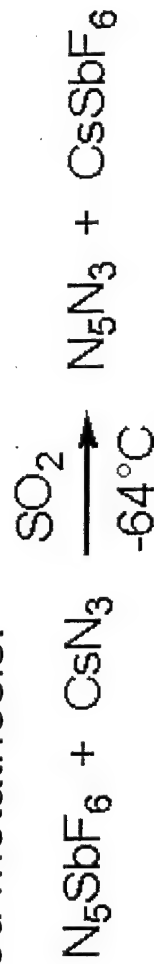


Conclusions concerning the stability of

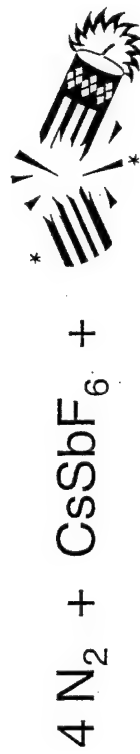


- Our results predict that $N_5^+N_3^-$ and $N_5^+N_5^-$ are unstable and decompose spontaneously with N_2 evolution.
- This conclusion was experimentally confirmed in our laboratory for $N_5^+N_3^-$

➤ Desired metathesis:

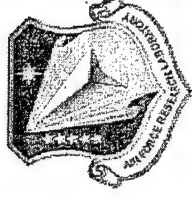


Obtained products:





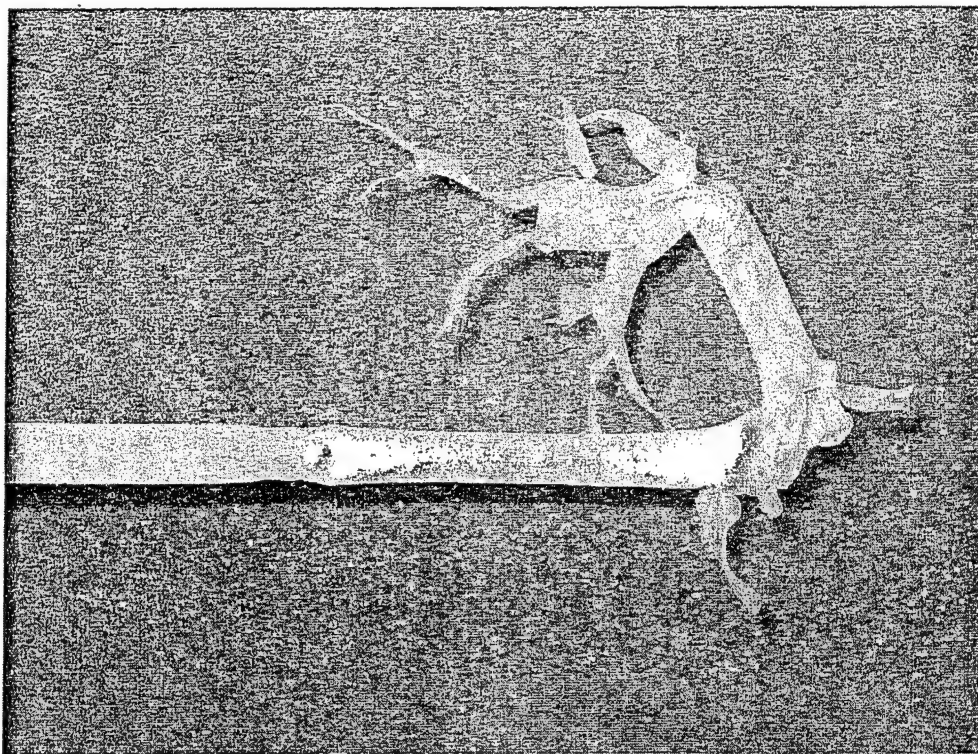
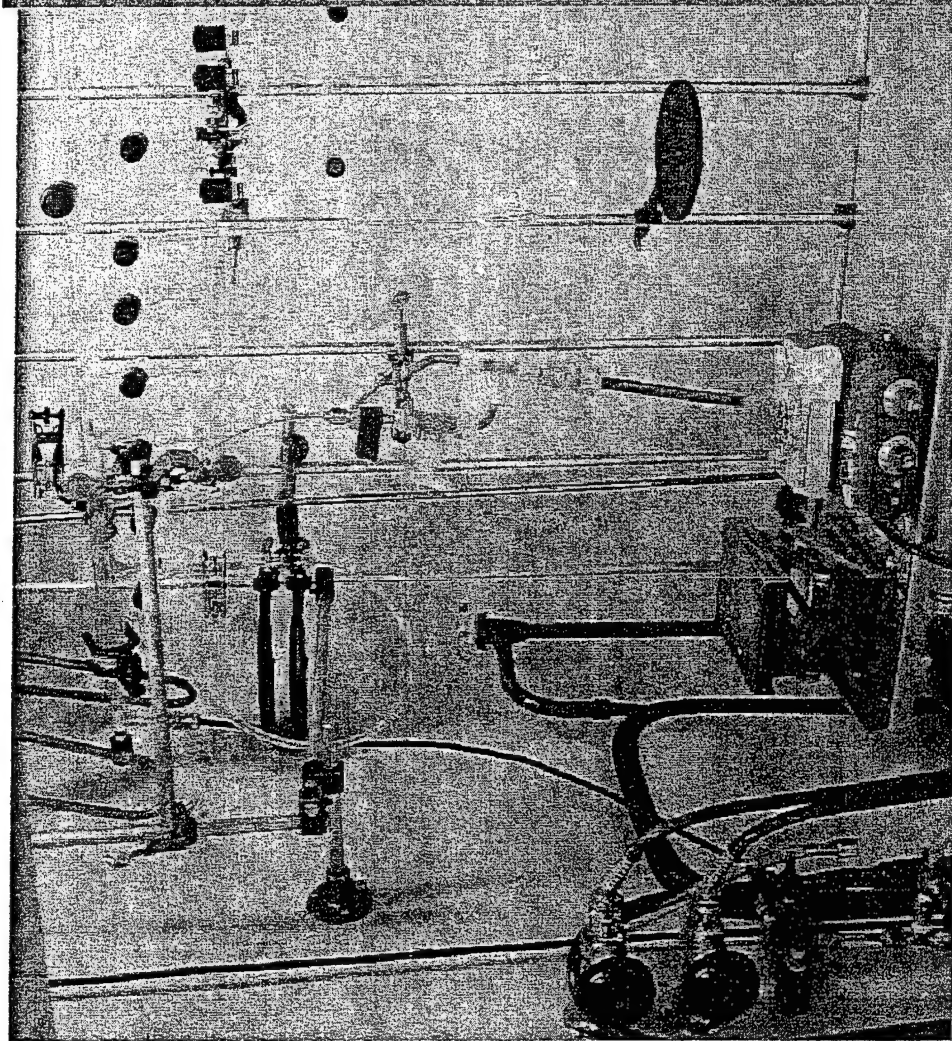
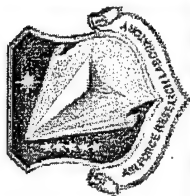
Polyazide Chemistry



- Complex azides have great potential for energetic high-nitrogen ingredients and as potential counter-ions for N_5^+
- Typical examples of compounds previously prepared by us:
 - $C(N_3)_3^+ClO_4^-$, $C(N_3)_3^+N(NO_2)_2^-$, and $C(N_3)_3^+NO_3^-$
- Compounds studied under this program include
 - $As(N_3)_3$, $Sb(N_3)_3$, $As(N_3)_5$, $Sb(N_3)_5$, $As(N_3)_6^-$, $Sb(N_3)_6^-$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $P(N_3)_6^-$, $B(N_3)_6^-$, $N_5^+[P(N_3)_6]^-$, and $Ti(N_3)_4$
- Most of these compounds are very sensitive, but some can be safely handled, particularly when combined with large counter-ions
- Their synthesis generally involves the reactions of the corresponding fluorides or chlorides with $(CH_3)_3SiN_3$ in suitable solvents, such as SO_2



How much damage can $\frac{1}{2}$ mmol of $N_5^+[P(N_3)_6]^-$ cause ?

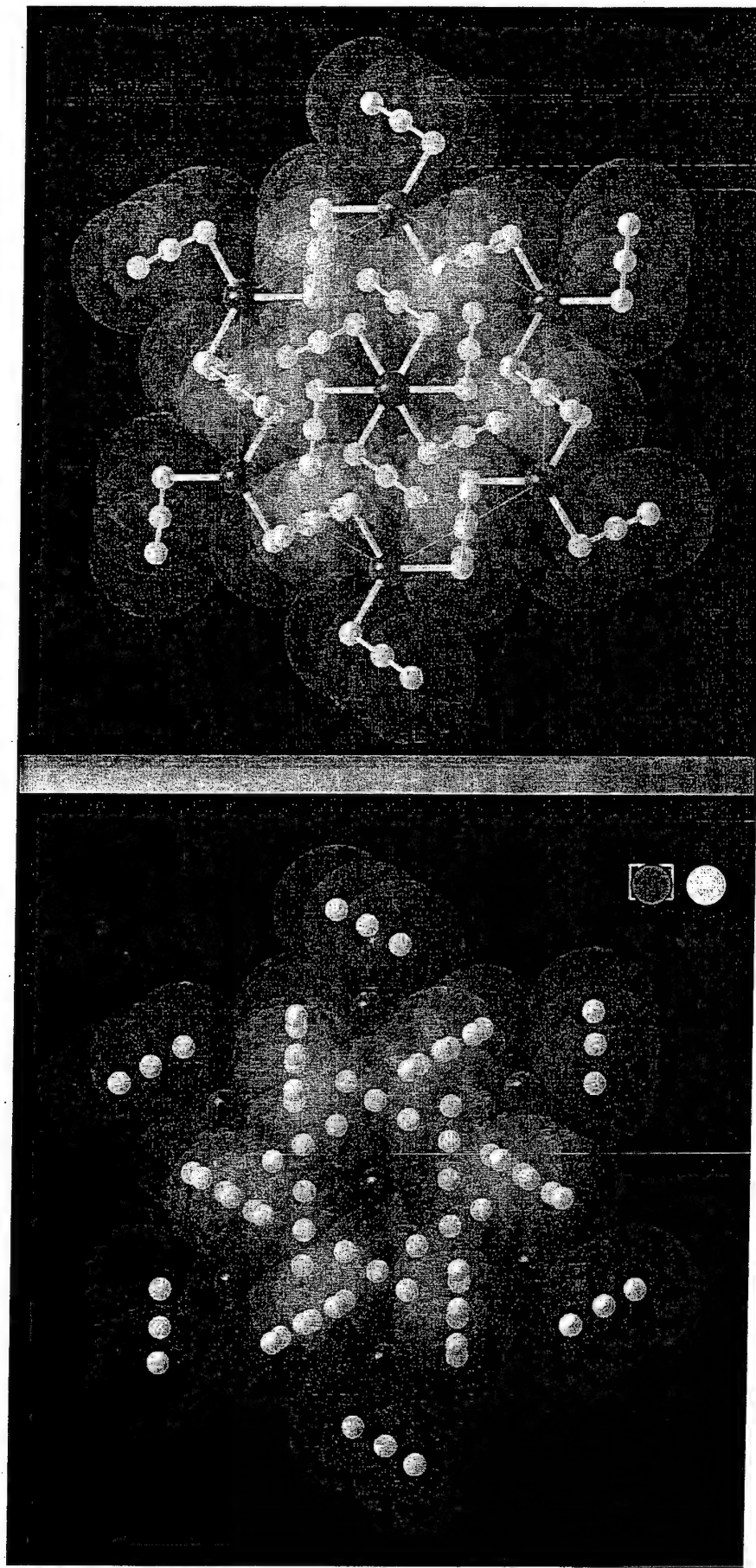
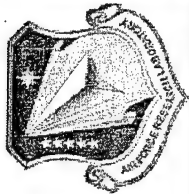


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Normal Polyazides

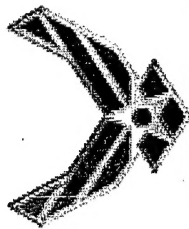


Covalent azides are normally strongly bent with M-N-N angles of about 120° , as shown here for $\text{Sb}(\text{N}_3)_3$

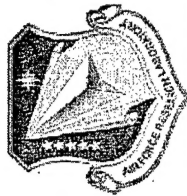
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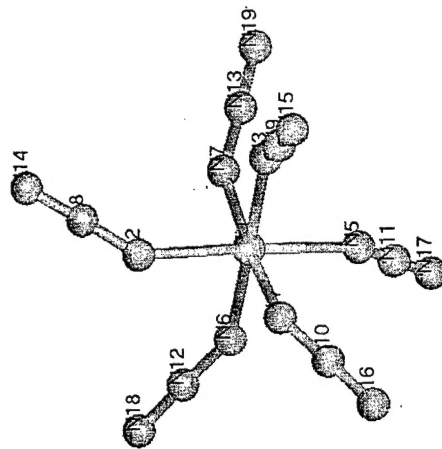
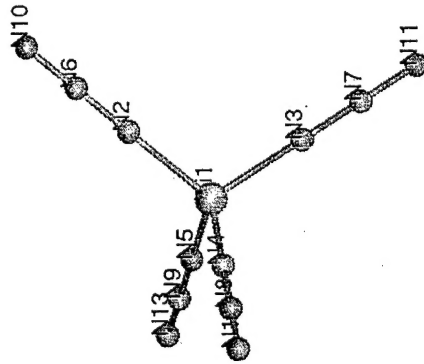
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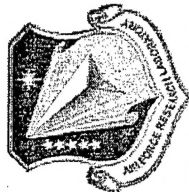
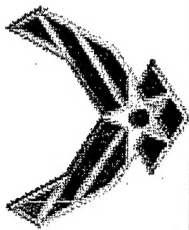


Novel type of covalent azides with linear M-N-N bonds



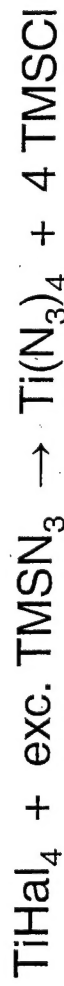
- Based on quantum chemical calculations, Gagliardi and Pyykkoe have recently predicted, (*Inorg. Chem.* **2003**, 42, 3074), for $\text{Ti}(\text{N}_3)_4$, $\text{Zr}(\text{N}_3)_4$, $\text{Hf}(\text{N}_3)_4$, and $\text{Th}(\text{N}_3)_4$ a novel type of bonding involving linear M-N-N bonds.
- We have confirmed these calculations for $\text{Ti}(\text{N}_3)_4$ and also predict that other azides, such as $\text{Fe}(\text{N}_3)_2$ (Melanie Teichert), can form linear M-N-N bonds. Based on our calculations, we also expect that the $\text{Ti}(\text{N}_3)_6^{2-}$ anion possesses the usual bent M-N-N bonds.





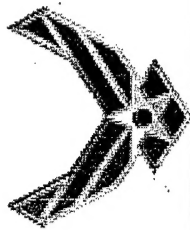
Synthesis and Characterization of $Ti(N_3)_4$

- Synthesis

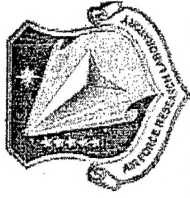


- Properties

- Yellow-orange solid
- Very shock-sensitive
- Very low volatility
- Raman spectrum and comparison with calculated spectra suggest that CN might be higher than 4 and Ti-N-N angle might be bent
- Need a gas-phase structure of free $Ti(N_3)_4$

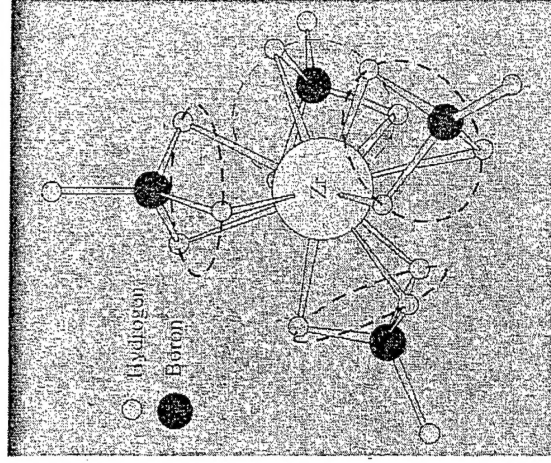


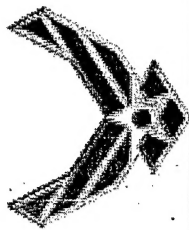
Possible explanations for linear M-N-N bonds



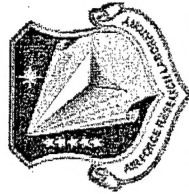
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- Gagliardi and Pyykkö invoke conjugation.
- We prefer the following interpretation because the calculated Ti-N bond distances are relatively long and are similar to single bonds. Also, the N_β - N_γ bonds are quite short, and the Ti-N-N bonds in $Ti(N_3)_6^{2-}$ are strongly bent.
 - The N_α atom of the $-N_3$ ligand has three free valence electron pairs which can act as a tridentate ligand and, in a tetrahedron, can perfectly overlap with three of the lobes of the Ti 3d-orbitals. This scheme is analogous to the structure of $Zr(BH_4)_4$ which possesses 4 trihapto BH_4 groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the N_α atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about 120° .





Conclusions



- The novel $N_5^+HF_2^-$ salt was prepared and serves as a useful reagent for the preparation of other N_5^+ salts.
- The reactions of NF_4^+ and $N_2F_3^+$ with HN_3 were studied. While NF_4^+ acted only as a fluorinating agent, one F of $N_2F_3^+$ was replaced by an azido group, but the substitution product was unstable and underwent rapid decomposition.
- The decomposition of complex fluoro salts of N_5^+ was studied both experimentally and computationally. It was shown that the life-time of FN_5 is very short and that under our reaction conditions only the expected decomposition products can be observed.
- In pursuit of a bulk synthesis for N_5^- salts, it was shown that the N_5^- anion can be prepared in solution and be observed by ^{15}N NMR.
- Reliable thermodynamic calculations were carried out for $N_5^+N_5^-$ and $N_5^+N_3^-$. It is shown that the previous use of vertical instead of adiabatic potentials led to very large errors and erroneous conclusions.
- Numerous polyazido compounds of P, As, Sb, Te, B, and Ti were prepared and characterized.
- $N_5^+[P(N_3)_6]^-$ was successfully prepared and characterized by low-temp. Raman.

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